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Design of a Graphite Element Drop-Tube Reactor System for Study of SO2 Removal by Injected Limestone Sorbents

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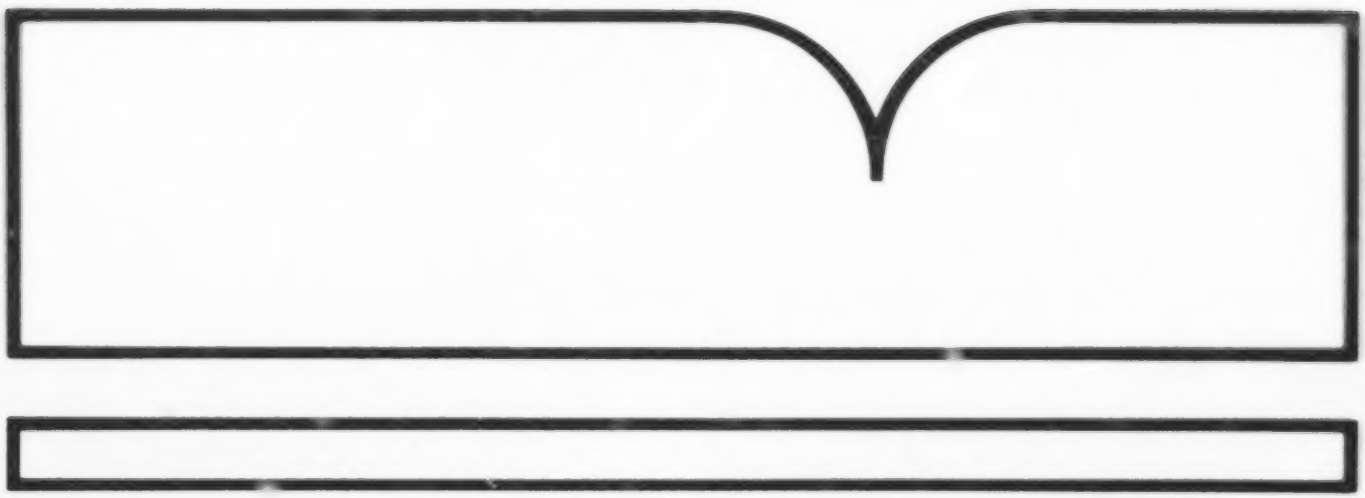

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16. ABSTRACT The article describes the design and operation of a graphite element drop-tube reactor system for a study of the fundamental mechanisms and reaction rates of SO2 removal by high-temperature injection of limestone-based sorbents. The reactor system is designed for laminar flow in an environment that allows for control of reaction temperature, s bent particle residence time, and atmosphere composition. The sorbent injection sy allows variable feed rates to as low as 1 mg/min. for particles as small as 1 eter in diameter. The water-cooled sorbent collection system arrests the high- ature reaction upon capture and allows analysis of the sorbent's efficiency of apture and in situ particle size distribution. The results presented show the reactivity of different types of sorbents at varying conditions of system operation.

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JOURNAL ARTICLE

Design of a graphite element drop-tube reactor system for study of SO_2 removal by injected limestone sorbents

Brian K. Gullett

U. S. Environmental Protection Agency, Air and Energy Engineering Research Laboratory, Research Triangle Park, North Carolina 27711

Gerry C. Snow and John A. Blom

Acurex Corporation, Research Triangle Park, North Carolina 27709

David A. Kirchgessner

U. S. Environmental Protection Agency, Air and Energy Engineering Research Laboratory, Research Triangle Park, North Carolina 27711

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The design and operation of a graphite element drop-tube reactor system for a study of the fundamental mechanisms and reaction rates of sulfur dioxide (SO_2) removal by high-temperature injection of limestone-based sorbents is described. The reactor system is designed for laminar flow in an environment that allows for control of reaction temperature, sorbent particle residence time, and atmosphere composition. The sorbent injection system allows variable feed rates to as low as 1 mg/min for particles as small as 1 μm in diameter. The water-cooled sorbent collection system arrests the high-temperature reaction upon capture and allows analysis of the sorbent's efficiency of SO_2 capture and *in situ* particle-size distribution. The results presented show the reactivity of different types of sorbents at varying conditions of system operation.

INTRODUCTION

The use of limestone-based sorbents for adsorption of and chemical reaction with gaseous sulfur dioxide (SO_2) has been studied extensively for use in reducing emissions from coal-fired power plants.[1] This technology is currently being studied by the U. S. Environmental Protection Agency in a program on limestone injection for multistaged burners (LIMB). When limestone, or calcium carbonate ($CaCO_3$), is injected into power plant boilers, its reactive form, calcium oxide (CaO), combines with gaseous SO_2 to form calcium sulfate ($CaSO_4$). This dry solid product can then be removed from flue gas streams by conventional particulate collection systems. More recently, attention has been focused on the use of hydrated lime, $Ca(OH)_2$, as a sorbent. Hydrated sorbents have greater reactivity than calcium carbonates, likely because of their very small particle size after the hydration process. However, hydrated sorbents are extremely prone to agglomerate, making particle feeding and sorbent reactivity measurement difficult at the laboratory scale.

Research in this process has required the development of high-temperature reactors to determine the fundamental reaction mechanisms and their rates of progression. These reactors must be capable of reaching the temperature range of 1000–1250 °C, in which the sulfation reaction is thermodynamically favorable. Isothermal reactor systems have been constructed using electrically heated, drop-tube furnaces with natural gas precombustors,[2,3] refractory-lined, natural-gas-fired furnaces,[4] and differential quartz-tube reactors with stationary sample holders.[5] These systems have various limitations, such as slow particle heat up, uncertainty of particle residence time, low temperatures and long residence times unrepresentative of field conditions, difficulty in testing/feeding micrometer sized particles, and sorbent deactivation by use of gaseous atmospheres that promote sintering.

The need for a reactor system to test the smaller hydrate particles under realistic temperature and flow conditions without adverse gas-promoted sintering effects led to the de-

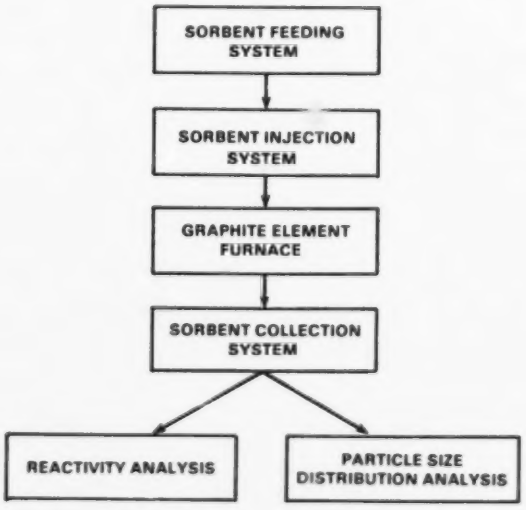

FIG. 1. Diagram of graphite furnace reactor system.

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velopment of a high-temperature, graphite furnace reactor (GFR) system. A GFR has been used[6] to study the composition of fly ash produced by the combustion of a lignite coal. In the research reported in this paper, a similar GFR with system modifications (Fig. 1) was applied to a new problem: measurement of the reactivity of calcium-based hydrated sorbents with SO_2.

I. DESIGN OF THE REACTOR SYSTEM

A. Graphite furnace

The primary component of the GFR system is an Astro model 1000A graphite element furnace. This instrument was configured to operate as a drop-tube furnace through modifications and construction of equipment based, in part, on previous work.[6] Although the electrically heated graphite elements are capable of maintaining temperatures up to 2000 °C, the present configuration is limited to 1850 °C by alumina and quartz components within the furnace. This provides peak temperature capability well above the thermodynamic limits of the sulfation reaction. The furnace operates at atmospheric pressure.

Figure 2 shows the principal components of the furnace. The top and bottom doors are machined from nickel-plated anodized aluminum and seal the process gas inlet port, sorbent injection probe, and collection probe. To provide a smooth flow path through the furnace and to protect the graphite heating elements from the reaction zone atmospheres, alumina muffle tubes were installed. The 61-cm-long outer muffle tube has a 7.94-cm outside diameter (o.d.)

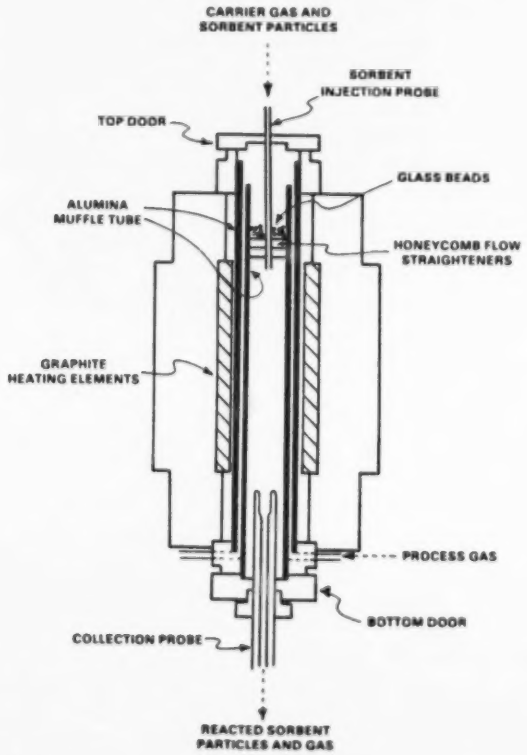

FIG. 2. Schematic cross section of the graphite furnace reactor.

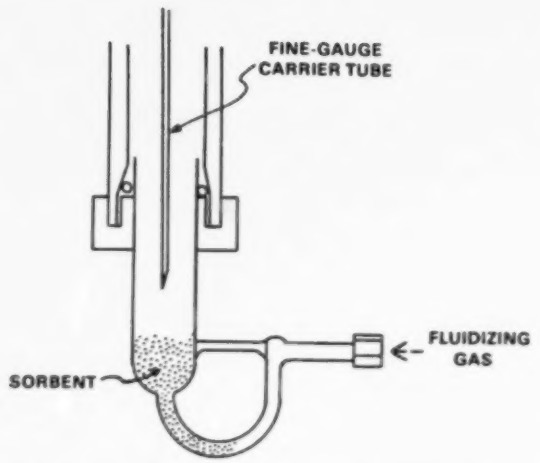

FIG. 3. Cross-sectional view of the sorbent feeder system.

and a 6.99-cm inside diameter (i.d.). The 61-cm-long inner tube is 6.03-cm o.d. and 5.40 cm i.d. The process gas is preheated by flowing between the inner and outer muffle tubes before it makes a 180° turn at the top of the furnace to enter the reaction zone.

The inner muffle tube has four ceramic ledges cemented to the inner walls 8.5 cm below the process gas entrance to support ceramic honeycomb flow straighteners. Two honeycombs having nominally 40 cells/cm^2 are used to eliminate flow turbulence and help preheat the process gas. A layer of 3-mm-diam Pyrex glass beads on top of the flow straighteners further evens the flow distribution across the reactor cross section. To ensure that small-scale turbulence is completely eliminated at the point of sorbent particle injection, the fine gauge injection tubing extends between 2.5 and 5.0 cm, approximately 20 cell diameters, below the honeycombs. Injected sorbent flows along the furnace center line through the reaction zone with the process gas. After passing through the furnace, the reacting sorbent particles are collected and quenched by a water-cooled sample collection probe. The probe may be raised or lowered along the furnace axis, which together with variations in the process gas flow, allows control of sorbent residence times in the furnace.

B. Particle feeder

The particle feeder system, shown in Fig. 3, is designed to uniformly feed sorbents with median particle diameters of under 2 μm while discouraging the formation and feeding of hydrate agglomerates. This is accomplished by a partially fluidized sorbent bed in which individual particles are entrained by the fluidizing gas stream. The entrained sorbent and carrier gas flow into a fine-gauge tube, above the sorbent bed. The particles and carrier gas are then axially injected into the main process gas within the reaction zone. The sorbent feed rate is varied by altering the position of the fine-gauge carrier tube above the bed.

The sorbent reservoir consists of a 50-mm o.d. Pyrex tube with a 25-mm o.d. U-shaped extension at the bottom. Individual reservoirs are used to hold a 0.5–1.0-g sample of each sorbent. The sorbent sample is fluidized by carrier gas

flowing through the U-shaped extension tube at 0.2 l/min. A vibrator agitates the reservoir to prevent channeling and to maintain homogeneity in the sample. The carrier gas and entrained sorbent particles enter the 1.2-mm i.d. carrier tube at the top of the reservoir and flow to a water-cooled probe for injection into the furnace. The gas velocity in the carrier tube is sufficient to maintain the suspension of sorbent particles and carry them to the injector probe without clogging. To eliminate dilution effects in the reaction zone, the fluidization/carrier gas has the same composition as the main process gas (typically 3000 ppm SO_2, 5% oxygen, balance nitrogen).

Sorbent feed rates may be adjusted between 1 and 20 mg/min. Lower rates are desired to minimize interparticle effect through, for example, localized depletion of SO_2. At a particle feed rate of 5 mg/min and a 5 l/min total flow of process gas containing 3000 ppm SO_2, the steady-state molar ratio of sulfur to calcium within the reactor is 7 : 1.

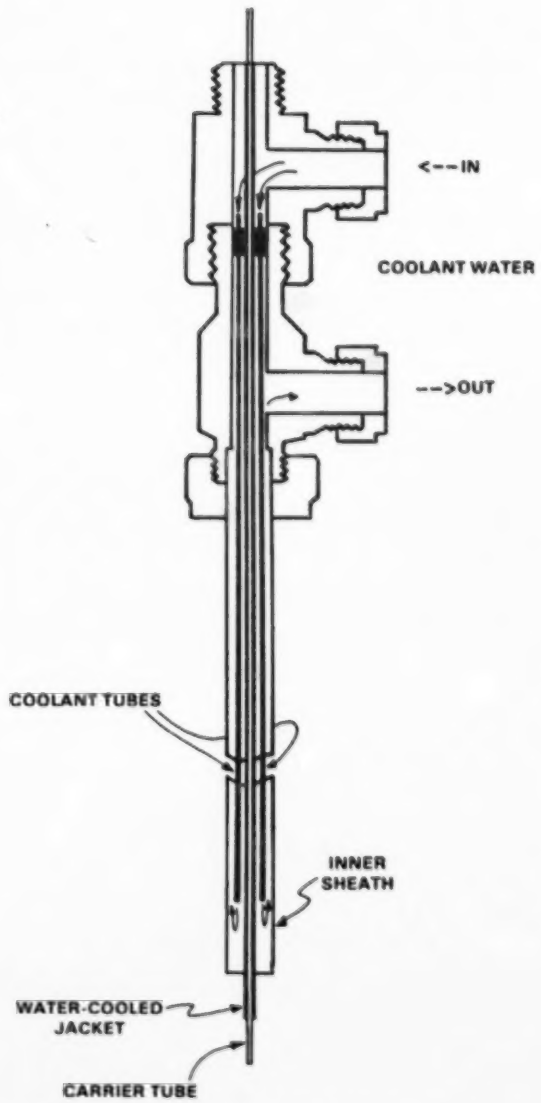

FIG. 4. Cross-sectional view of the sorbent injector probe.

C. Injection probe

Figure 4 is a diagram of the sorbent injector probe. The probe consists of a 3.2-mm-o.d. by 2.0-mm-i.d. stainless-steel inner sheath surrounded by an 8-mm-o.d. by 7-mm-i.d. stainless-steel water-cooled jacket. The inner sheath extends 50 mm below the water-cooling jacket. When inserted into the furnace, the water jacket terminates at the top of the honeycomb flow straighteners. The inner sheath extends 25 mm below the bottom of the flow straighteners into the furnace hot zone.

The 1.2-mm-i.d. carrier tube is inserted into the inner sheath of the probe. The position of the carrier tube is adjustable so that it may be extended up to 50 mm below the honeycomb flow straightener. At this location, minor flow disturbances generated by the honeycomb elements have been damped. The carrier tube may also be removed between runs for cleaning and to reduce its exposure to furnace temperatures.

D. Collection probe

After passing through the furnace reaction zone, the sorbent particles are collected by a quartz sample probe. The probe and collection system are shown in Fig. 5. To provide a

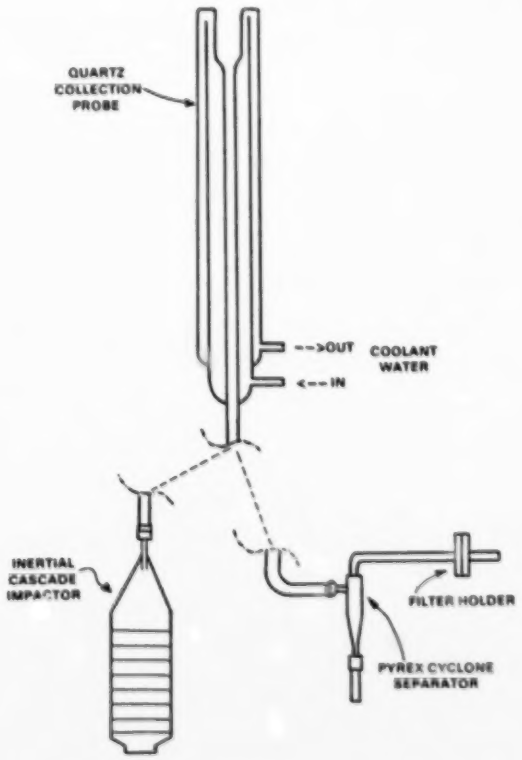

FIG. 5. Schematic of the collection probe with options for total solids collection with a cyclone or particle size analysis with an inertial cascade impactor.

rapid quench of ongoing reactions, the probe design incorporates water-cooled walls and a provision for the injection of nitrogen diluent. All of the process gas and sorbent exit the reactor through the collection probe. At the probe entrance, a cooling rate of up to 10 000 °C/s is achieved, dropping the sample temperature to approximately 500 °C within 50 ms.

A small Pyrex cyclone separator and a stainless-steel filter holder with a glass microfiber filter are used to capture the sorbent samples at the outlet of the collection probe. Alternatively, the reacted sorbent particles can enter an in-line inertial cascade impactor, where they are classified by aerodynamic size, from ~35 to ~0.5 μm. Thermocouples attached to the cyclone and filter housings are used to monitor their temperatures. The total gas flow through the probe is measured downstream of the filter by a glass tube rotameter.

E. Analysis

The solid reacted sorbent collected on the inertial impactor stages or by the cyclone/filter system is analyzed for extent of reaction by determining the concentration of calcium ions, Ca^{2+}, and sulfate ions, SO_4^{2-}. The calcium is determined by atomic absorption spectroscopy, and the sulfate is analyzed by ion chromatography. The particle size distribution of the sorbent is determined by the weight gain on each stage of the impactor, each stage acting to collect particles within a certain size range. Coulter counter analysis and/or scanning electron microscopy can be used to support the results obtained by the inertial impactor.

II. EXPERIMENTAL PROCEDURES

To begin operation, the GFR is turned on and adjusted to a reactor temperature of 1000 to 1250 °C. When system temperatures, gas flow rates, and pressures stabilize, a sorbent reservoir is installed in the fluidized feeder system and injection is started. A typical run requires 30–60 min to feed ~50–500-mg sorbent, depending on the type of sorbent and the rate of carrier gas flow. At the collection cyclone and filter, typical sample recovery rates are 70%, with the remaining sorbent adhering to the collection probe walls. Between system tests the GFR system is extensively flushed with nitrogen jets to remove any remaining sorbent. Samples collected in the cyclone vial are capped at the end of a run, stored under vacuum, and analyzed for calcium and sulfate. Alternatively, each stage of the inertial impactor is removed and immediately placed in covered petri dishes for subsequent weighing.

III. CHARACTERIZATION OF REACTOR

Typical temperature profiles for the furnace reactor zone are shown in Fig. 6. Although end effects are not insignificant, the temperature encountered by the sorbent passing through the reaction zone (the region in which the temperature is at or above 850 °C) is generally within 100 °C of the mean set-point temperature. Temperature profiles are measured for each combination of furnace set-point temperature, process gas flow rate, and sample collection probe location used in the sulfation studies. This information is collected by traversing a type-R (platinum against platinum with 13% rhodium) thermocouple probe along the sorbent flow path on the furnace axis. The thermocouple was fabricated from 0.38-mm-diam wire and has a 0.64-mm-diam uncoated bead.

The temperature measurements shown in Fig. 6 are uncorrected for radiation error. Thus the indicated temperature will be slightly higher than the true gas temperature because of the radiative input from the muffle tube. The

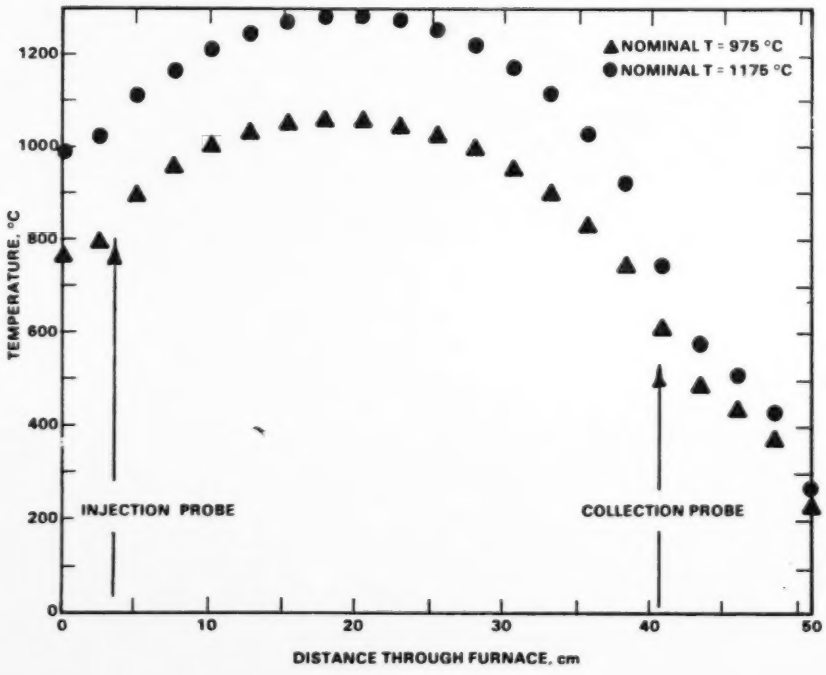

FIG. 6. Center-line temperature profiles in the graphite furnace for nominal temperatures of 975 and 1175 °C and operating conditions that result in a sorbent residence time of 1.6 s.

average temperature of the inner muffle tube is calculated to be less than 40 °C above the nominal reaction zone temperature. Heat transfer analyses show the error to be 1%–2% at indicated temperatures of 950–1200 °C, respectively.

The nominal reaction zone temperature is calculated by taking a weighted mean in the region where the temperature is above 850 °C between the sorbent injection and collection points. Nominal reaction zone temperatures for the current research program fall between 950 and 1200 °C. Heat transfer calculations show that the sorbent particles reach the temperature of the surrounding gas within 0.0001 s of injection into the furnace.

The main process gas flow rate generally ranges from 5 to 10 l/min giving typical reactor Reynolds numbers between 50 and 100. This ensures that the reactor flows are completely laminar and that the injected sorbent stream remains on the reactor center line. Visual observation of the radial sorbent dispersion at the end of the reactor confirms that the sorbent follows the axial center line. This flow regime gives ease of sample recovery by the collection probe and allows an accurate definition of sorbent particle residence times within the reactor.

Under nominal operating conditions, sorbent particles are injected into the reactor at velocities ranging from 3 to 6 m/s with coflowing process gas at average velocities of 0.15–0.35 m/s. For 2-μm particles at nominal reactor temperatures, the particle Reynolds number is on the order of 0.1. Under these conditions, the drag force acting on the particle may be calculated using Stokes' law, $C_D = 24/\mathrm{Re}$, where Re is the particle Reynolds number and C_D is the coefficient of drag defined as

$$C_D = 2F_D/A_P \rho V^2, \tag{1}$$

where F_D is the drag force, A_P is the cross-sectional area of the particle, ρ is the density of the process gas at reactor conditions, and V is the differential velocity between the particle and the surrounding process gas. Drag force calculations show that the velocity of an injected particle will equilibrate to the surrounding gas velocity within 0.0001 s, or approximately 0.25 mm from the injector. Further calculations show the terminal settling velocity of the particles in the process gas to be 0.0001 m/s or about 0.03%–0.07% of the average gas velocity in the reactor.

Given the above description of particle dynamics, it is assumed that the average process gas velocity through the reactor can be used to provide a qualitative indication of sorbent residence time within the reactor. In any case, the resulting sorbent residence time calculation is considered accurate enough for comparisons between runs if not for an absolute indication. Residence time is adjusted by varying the process gas flow rate and/or the position of the sorbent collection probe. Residence times between 0.2 and 2.0 s are available.

IV. PRELIMINARY RESULTS

Tests of sorbent reactivity in the GFR system were conducted with three different sorbents: a dolomitic pressure-hydrated lime (Ivory Finish Lime) from United States Gypsum Company, and two calcitic atmospheric-hydrated limes (Longview and Linwood) from Longview Lime Company and Linwood Lime and Cement Company, respectively. Gravity sedimentation analyses of these sorbents showed mass median diameter values (D_{50}) of 5, 4, and 2 μm for Ivory, Longview, and Linwood, respectively.

TABLE I. Sorbent reactivity measured as percent CaO conversion to $CaSO_4$ at nominal temperatures of 975 and 1175 °C and SO_2 concentrations of 2300 ppm with sorbent feed rate varying between 6 and 12 mg/min.

Sorbent	Percent conversion of calcium 975 °C*	1175 °C*
Ivory	14.3	29.1
Longview	9.1	16.8
Linwood	11.8	21.1

* Nominal furnace temperature.

Each of the sorbents was tested for reactivity at nominal system temperatures of 975 and 1175 °C. The average velocities of the process gas stream at the nominal reaction zone temperatures of 975 and 1175 °C were 0.19 and 0.22 m/s, respectively. The length of the reaction zone was 0.305 m at 975 °C and 0.356 m at 1175 °C, yielding a sorbent particle residence time of 1.6 s at both sets of operating conditions.

The process gas was composed of molecular nitrogen with 2300 ppm SO_2 and 5% O_2. Sorbent feed rates varied between 6 and 12 mg/min yielding steady-state molar ratios of sulfur to calcium in the reactor between 3.6 and 7.1. The results and conditions of the testing are outlined in Table I. The results illustrate the reactivity or percent calcium conversion to $CaSO_4$, under the different furnace conditions with the three sorbents. The standard deviation of the results did not exceed 2.2% conversion, reflecting the precision of the system and analyses.

Testing with two of these same sorbents in large pilot-scale reactors has exhibited the same order of sorbent utilization.[7] Limited results from bench-scale, gas-fired, isothermal system[8] tests of the Linwood and Longview sorbents have yielded from 16% to 23% utilization of calcium between 1050 and 1200 °C. These results are consistent with the range of utilizations found in the research reported here at 1175 °C. However, unlike our work, they found higher utilizations at the lower temperatures. The discrepancy between these results is likely because of differences in the temperature profiles of the reactors. This causes changes in the rates of sorbent activation and sintering which affect reactivity.

Data from one of the sorbents, Linwood, were obtained from the inertial impactor, resulting in the *in situ* particle size distribution seen in Fig. 7. The particle size distribution as fed by the particle feeder system is typically quite different from that obtained by gravity sedimentation analysis with the use of dispersing agents. The D_{50} value changed from 2 μm with the gravity sedimentation to 20 μm with the impactor, illustrating the degree of hydrate agglomeration.

The GFR system allows experimental control over reaction conditions of time, temperature, gas atmosphere, and sorbent feed rate. This provides a means of measuring the reactivity performance and *in situ* particle size distribution of different sorbents for use in controlling SO_2 emissions.

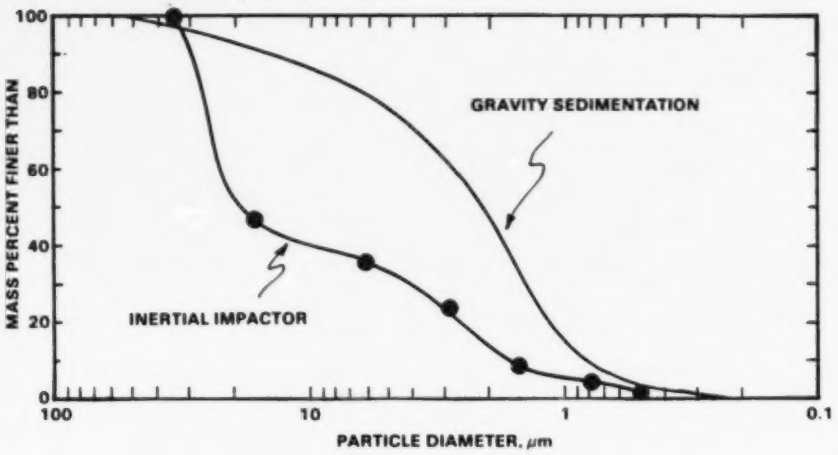

FIG. 7. Particle size distribution of Linwood sorbent from the inertial cascade impactor at a reactor temperature of 21 °C and from gravity sedimentation.

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